On the positivity of entropy production in multiphase systems

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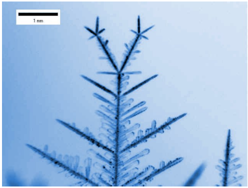
July 3, 2019

Multiphase chemical systems are everywhere

Liquid-gas reactions



Crystal growth processes

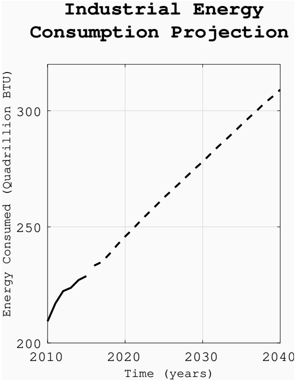
The atmosphere

We call a system where matter exists simultaneously
in two or more states of aggregation a multiphase system

Multiphase operations consume 10% of the world's energy

Challenges in process systems:

- Energy demands could be incremented by 48% in 2040
- The dynamical properties of multiphase systems are still not fully understood



Source: eia.gov

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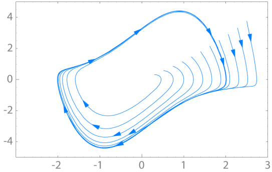
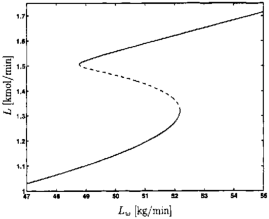


Limit cycles



Steady state multiplicity

Can we use thermodynamics to establish
the stability properties of multiphase systems?

Outline

Convexity properties of thermodynamic systems
- Limitations in multiphase systems

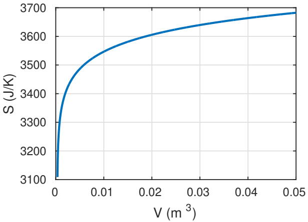
Internal entropy production in multiphase systems
- Compartmental modeling

On the positivity of internal entropy production
- Internal entropy production as a Lyapunov function candidate

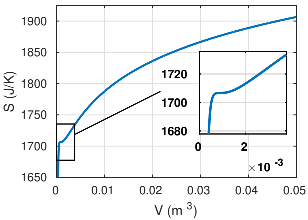
Phenomenological interpretation of the obtained results
- Stable temperature profiles
- Stable mass concentration profiles

Conclusions and future work perspectives

Thermodynamics allows for a better understanding of chemical processes



Entropy for a single phase system



Entropy for a multiphase system

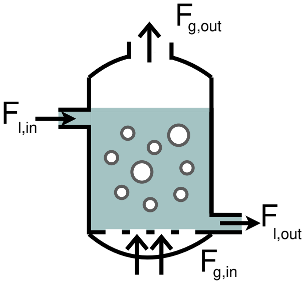
How can we characterize the stability properties of multiphase systems?

Every physicochemical system produces entropy at a rate

$$\dot{\Sigma} = \dot{\Sigma}_e + \dot{\Sigma}_i$$

where

- $\dot{\Sigma}_e$ is the environmental entropy production, and
- $\dot{\Sigma}_i$ is the internal entropy production.

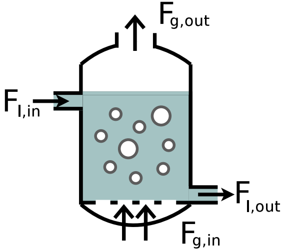


Liquid-gas reactor

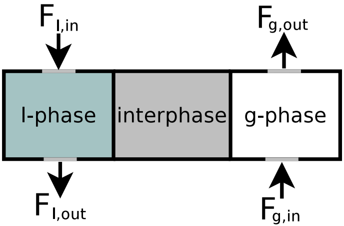
Second Law of Thermodynamics

$$\dot{\Sigma}_i \geq 0$$

A compartmental approach to modeling multiphase systems



Liquid-Gas Reactor



Abstract Multiphase System

Internal flows increase the amount of entropy in multiphase systems

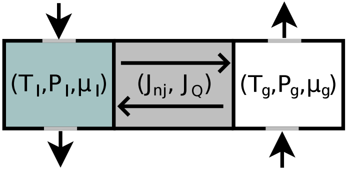
Spatial inhomogeneities

$$\left[T_l,\ P_l,\ \mu_l\right] \neq \left[T_g,\ P_g,\ \mu_g\right]$$

are known to cause:

- Mass and
- Energy

to move between subsystems at a rates J_{nj} and J_Q (J/sec).



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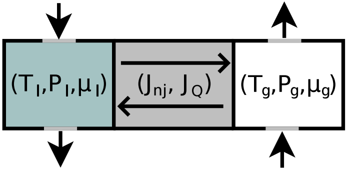


Internal flows (J_{nj}, J_Q) are known to produce entropy at a rate

$$\Sigma_\imath = \sum_{\jmath=1}^{c} J_{nj}\, X_{nj} + J_Q\, X_Q,$$

where (X_{nj}, X_Q) are known to be the driving forces behind flows (J_{nj}, J_Q).

Internal entropy production model

Energy, mass and momentum balances can be represented as a non-linear system of differential algebraic equations

$$\frac{d}{dt}\begin{bmatrix}\zeta_l \\ \zeta_g\end{bmatrix} = \begin{bmatrix} f_l(\zeta_l, \zeta_g, w) \\ f_g(\zeta_l, \zeta_g, w)\end{bmatrix}$$

$$0 = g(\zeta_l, \zeta_g, w)$$

where the Jacobian $\partial g / \partial w$ is non singular.

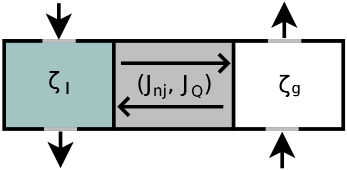
Given state functions

$$\zeta \mapsto (J_{nj},\, X_{nj},\, J_Q,\, X_Q)$$

the system produces entropy as described by

$$\Sigma_{\imath} = \sum_{\jmath=1}^{c} J_{nj}\, X_{nj} + J_Q\, X_Q,$$

[Romo-Hernandez et al. 2018]



Entropy production behaves numerically as a Lyapunov function

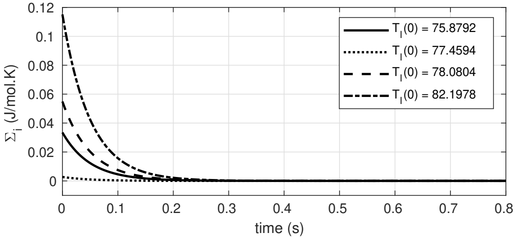


Figure: $\Sigma_\imath$ vs t, for a methanol-water liquid-vapor system initialized far from thermodynamic equilibrium ($T_{eq} = 78.09^o$C)

Result

Numerical evidence shows that

$$\Sigma_\imath = \sum_{\jmath=1}^{c} J_{nj}\, X_{nj} + J_Q\, X_Q,$$

behaves like a Lyapunov function for the equilibrium state $\zeta^\star$.

Following the numerical results, we investigate if $\Sigma_\imath$ is a Lyapunov function

To show that

$$\Sigma_\imath(\zeta) = \sum_{\jmath=1}^{c} J_{nj}\, X_{nj} + J_Q\, X_Q \tag{1}$$

is a Lyapunov function candidate to characterize the stability of equilibrium $\zeta^\star$ in multiphase systems, we demonstrate that:

1. The internal entropy production (1) is zero at $\zeta^\star$.
2. The internal entropy production (1) is positive when $\zeta \neq \zeta^\star$.

Writing the internal entropy production using alternative flows and forces

Internal entropy production rate

$$\Sigma_\imath = J_Q\, X_Q + \sum_{\jmath=1}^{c} J_{nj}\, X_{nj},$$

where $J_Q := \sum_{j=1}^{c} J_{nj}\, \bar{h}_{lj} + \lambda_{li} \delta T_l$.

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$$\Sigma_\imath = \lambda_{li}\, \delta T_l\, X_e + \sum_{\jmath=1}^{c} J_{nj}\left(X_{nj} + \bar{h}_{lj}\, X_e\right)$$

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where

$$\begin{aligned} X_{nj} + \bar{h}_{lj}\, X_e &= -\frac{1}{T_l}(\mu_{gj} - \mu_{lj})\big|_{T_l} \\ &= -R\ln\left(\frac{y_j}{x_j\gamma_j}\right) + R\ln\left(\frac{f_{lj}}{P_l}\right), \end{aligned}$$

and f_{lj} and γ_j represent the fugacity and activity coefficient of component j.

Alternative flows and forces

Alternative Flows and Forces

Internal entropy production for a two phase system

$$\Sigma_{\imath} = J'_Q\, X'_Q + \sum_{\jmath=1}^{c} J'_{nj}\, X'_{nj}. \tag{2}$$

where

$$X'_Q = T_l - T_g, \quad J'_Q = \lambda_{li}\, \frac{\delta T_l}{T_g\, T_l} \qquad J'_{nj} = R J_{nj}, \quad X'_{nj} = \ln\left(\frac{y_j^\star}{y_j}\right).$$

Note that

$$y_j^\star = K_{lj}\, x_j := \frac{\gamma_j(x) P_j^{sat}(T_l)}{P_l} x_j,$$

represents the gas composition in the system at equilibrium.

Internal entropy production is zero at equilibrium I

Equilibrium

The thermodynamic equilibrium state is defined as a state $\zeta^\star$ such that

$$0 = \mu^\star - \mu_{gj}(P, T, y_1, \dots, y_c)\big|_{\zeta^\star}$$
$$0 = \mu^\star - \mu_{lj}(P, T, x_1, \dots, x_c)\big|_{\zeta^\star}$$
$$1 = \sum_{k=1}^{c} x_k\big|_{\zeta^\star} = \sum_{k=1}^{c} y_k\big|_{\zeta^\star}$$

where $j = 1, \dots, c$.

Remark

Assuming that solutions of the equilibrium state are unique, pressure, temperature and composition in a multiphase system at equilibrium satisfy

$$\left.\begin{aligned} P_i &= P_l = P_g \\ T_i &= T_l = T_g \\ x_{ij} &= x_j \\ y_{ij} &= y_j \end{aligned}\right\} \text{Spatial Homogeneity}$$

Internal entropy production is zero at equilibrium II

Theorem 1:

Let $\zeta^\star$ stand for the equilibrium state for a multiphase where concentration in the gas y_j and concentration in the liquid x_j fulfill:

$$y_j - x_j \neq 0 \; \forall j.$$

Let

$$\Sigma_\imath(\zeta) = \sum_{\jmath=1}^{c} J_{nj}(\zeta)\, X_{nj}(\zeta) + J_Q(\zeta)\, X_Q(\zeta)$$

represent the internal entropy production. Then $\Sigma_\imath(\zeta^\star) = 0$.

Proof.

The proof follows from showing that interface flows (J_{nj}, J_e) and conjugated driving forces (X_{nj}, X_e) are zero at $\zeta^\star$ as a consequence of spatial homogeneity at equilibrium.

Theorem: Positivity of internal entropy production I

Definition

Let $f = [f_1,\ f_2]^{\mathrm{t}}$ depend on the deviation from equilibrium

$$f_1(\zeta) = (T_l - T_i) \cdot (T_i - T_g)$$
$$f_2(\zeta) = \left(y_j^\star - y_j\right) \cdot \phi(\zeta)$$

where $y_j^\star$ represents the gas equilibrium concentration

$$y_j^\star = K_{lj}\, x_j,$$

and where $\phi(\zeta)$ is a function that depends on the molar transport

$$J_n(\zeta) = \frac{\beta_l\left(x_j - x_{ij}\right) - \beta_g\left(y_j - y_{ij}\right)}{y_j - x_j}.$$

Let

$$g(\zeta) = K_{lj} - y_{ij}/x_{ij},$$

where $K_{lj} = K_j(\zeta_l)$ stands for the multiphase equilibrium partition ratio.

Theorem: Positivity of internal entropy production II

Theorem 2:

Let ζ represent the state for a multiphase system. Let the thermodynamic variables be defined as a function

$$\zeta \mapsto (T_\alpha, P_\alpha, x_1, y_1, \ldots, x_c, y_c, x_{i1}, y_{i1}, \ldots, x_{ic}, y_{ic}, J_n),$$

where the output represents temperature, pressure, molar composition, and interface transport, respectively.

There exists a domain of thermodynamic consistency

$$\Theta_0 := \left\{\zeta \,\middle|\, f(\zeta) \geq 0, \text{ and } g(\zeta) = 0\right\},$$

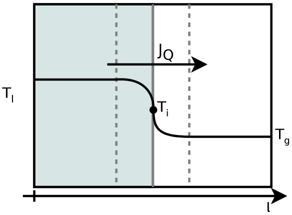
such that

$$\Sigma_\imath(\zeta) > 0 \quad \zeta \in \Theta_0$$

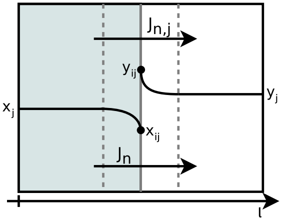
where

$$\Sigma_\imath(\zeta) = \sum_{\jmath=1}^{c} J_{nj}\, X_{nj} + J_Q\, X_Q.$$

Theorem 2 has clear phenomenological implications



Multiphase Temperature Profile



Multiphase Mass Profile

Results from Theorem 2:

- Non-equilibrium systems where temperature profiles change monotonically are consistent with the second law.
- There is a finite number of molar concentration profile configurations in multiphase systems far from thermodynamic equilibrium.

Conclusions and future work I

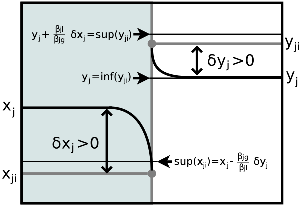
On the positivity of entropy production

We have shown that it is possible for a multiphase system to operate far from equilibrium while having a positive internal entropy production.

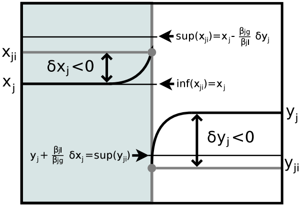
Future Work

- What are the conditions such that entropy production decreases in time along the dynamics of multiphase systems?
- Can our methodology be extended to azeotropic systems and to liquid-vapor processes with multiple equilibria?

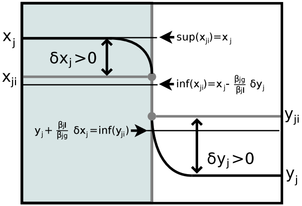
Appendix: 12 feasible concentration profiles I



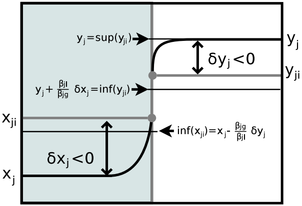
Profile p1



Profile p2

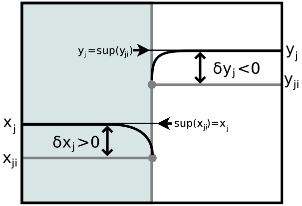


Profile p3

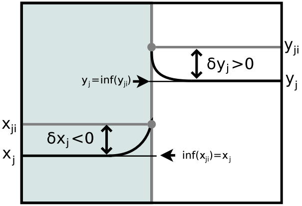


Profile p4

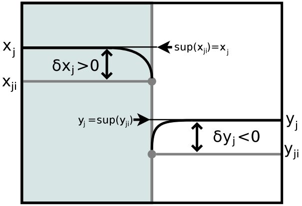
Appendix: 12 feasible concentration profiles II



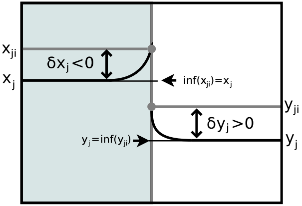
Profile p5



Profile p6

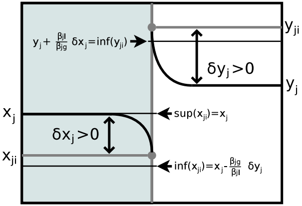


Profile p7

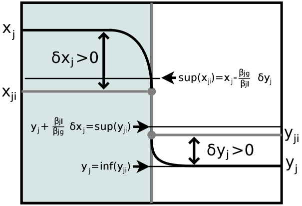


Profile p8

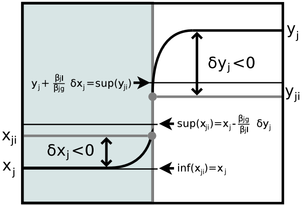
Appendix: 12 feasible concentration profiles III



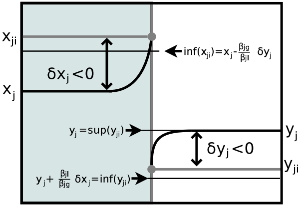
Profile p9



Profile p10



Profile p11



Profile p12